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CATHODE EFFECTS IN THE DIELECTRIC BREAKDOWN OF LIQUIDS

by

J. K. Bragg, A. H. Sharbaugh, and R. W. Crowe

Report No. RL-953 September 1953

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ABSTRACT
The apparent (measured) electric strength of a liquid dielectric depends on the nature of the cathode used. The field emission of electrons from the metallic cathode is assumed to be responsible for this effect; it may provide space charge which distorts the electric field in the dielectric. The nature of the cathode determines the range of electric fields over which the emission becomes appreciable. In this paper we discuss in detail the emission of charge and the formation of space charge. Because of theoretical and experimental uncertainties connected with supposedly uniform metallic surfaces, an electrode consisting of an electrolyte solution is also considered. Although the experimental results demonstrate that ions are emitted from such cathodes under the influence of strong electric fields, the role in providing space charge is similar to that of metal electrodes that emit electrons.

For the former electrode, the considerations regarding space-charge formation predict a definite dependence of apparent electric strength on electrolyte concentration and provide a way of testing the basis of the theory. Certain experiments reported here confirm this prediction.

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CATHODE EFFECTS IN THE DIELECTRIC BREAKDOWN OF LIQUIDS

J. K. Bragg, A. H. Sharbaugh, and R. W. Crowe

I. INTRODUCTION

The influence of the nature of the cathode metal upon the breakdown of dielectrics has been observed by many investigators. Von Hippel and Alger(1) first attributed this effect, as observed in the study of alkali halide crystals, to field emission of electrons from the cathode. Evidence that the origin of the effect in liquids is also field emission was found by Salvage,(2) who succeeded in showing a rough correlation between his experimental results and the vacuum work function of the metal used as cathode. Because of the sensitivity of the electron emission characteristics of a metal to the physical and chemical condition of its surface, however, such correlations are at best qualitative, and may be difficult to reproduce.

We have tried to put the suggestion of von Hippel in a quantitative form, and have designed a new kind of breakdown experiment to give a reliable test of the resulting theory. The experiment involves the use of a cathode consisting of an aqueous solution of electrolyte; the emission of ions from this cathode is a reproducible phenomenon whose dependence upon electrolyte concentration can be predicted. The theory depends on a distortion of the electric field, which may be caused by the emission of charge from the cathode into the dielectric.

For example, if an electric field of 10^6 volts/cm is impressed on a dielectric, field emission of electrons from a metal cathode may occur as shown by Le Page and Dubridge.(3) This emission may provide a considerable density of negative charge in the gap between electrodes. The amount of such charge that can be transported across the gap to the anode is limited by the properties of the dielectric (the mobility it allows the charges, and the dielectric constant) and by the geometry of the gap. The current that flows is therefore dependent on cathode properties at low fields; but when the field is high enough to cause strong emission, the current becomes independent of the nature of the cathode, and is prescribed by the properties of the gap through which the charge must be transported.

In the latter case, a nonuniform distribution of space charge arises, and the electric field in the gap becomes inhomogeneous. It is to this feature that the cathode effects are ascribed; that is, under these "space-charge-limited" conditions, the electric field in a region of the dielectric is enhanced to a magnitude considerably greater than the average (measured) field. The value of the average field at which this occurs is, however, dependent on the nature (emission characteristics) of the cathode.

The connection of this with breakdown strength measurements must be made with the help of a somewhat arbitrary assumption. We first suppose that the intrinsic electric strength of a dielectric is a meaningful property. We define it in terms of the magnitude of the homogeneous electric field, existing in a region of the dielectric, necessary to disrupt this region or to establish a conducting path across it, initiating processes from outside the region being excluded. The region considered must be large enough so that the property so defined is independent of the size of the region.

The intrinsic electric strength, defined in this way, obviously depends only on the nature of the dielectric; what is usually measured does not. Its relation to cathode effects is the subject of our basic assumption. We assume that a dielectric will break down whenever the average electric field over a region of dimension δ in the direction of the field becomes equal to the intrinsic electric strength, the magnitude of δ being just that for which the homogeneous electric field necessary for disruption of the region becomes independent of δ.

It should be noticed that this assumption is independent of the nature of the breakdown process, and all the conclusions we draw from it will apply, whatever the breakdown mechanism. However, the understanding of breakdown mechanisms and the techniques of measurement are not yet sufficiently advanced to make this hypothesis operationally useful. We will consequently use a somewhat indefinite idea; we ask simply that the electric field become equal to the intrinsic strength somewhere in the dielectric.

In the remainder of this paper, we will develop the consequences of the assumptions set forth above and report the extent to which these ideas are supported by experiment.

II. MECHANISMS OF CHARGE EMISSION

A. Field Emission

Evidence that the high-field emission current from metal cathodes into dielectrics is essentially field emission has been given by Le Page and Dubridge.(3) They measured the emission current into toluene as a function of field strength and temperature. Figure 1 shows some of their results, plots of the logarithm of the current against reciprocal temperature for various field strengths. It will be observed that the magnitudes of the slopes decrease as the field strength is increased. This suggests the gradual transition from Schottky emission, which has a pronounced exponential temperature-dependence, to field emission, which is independent of temperature. The electric fields with which we deal are greater than any listed in this diagram.

Field emission into the vacuum is described fairly well by the Fowler-Nordheim equation(4),

$$j = f(\chi)\, E^2 \exp(-b\chi^{3/2}/E). \qquad (1)$$

Here b is a constant, χ is the vacuum work function, and E is the electric field. The quantity $b\chi^{3/2}$ is of the order of 10^8 if E is expressed in volts per centimeter, so that this expression describes a current that increases very strongly in the region around 10^7 volts/cm. The quantity $f(\chi)$ is usually of such a magnitude that appreciable emission appears at about 10^7 volts/cm. The applicability of the law depends on the presence of uniform surfaces; in general, the presence of points and patches must be taken into account.

If the emission is into a dielectric, the situation is not so clear. If the dielectric may be regarded as structureless, one may derive the equation(3)

$$j = f^*(\chi^*)\, E^2 \exp(-b^*\chi^{*3/2}/E). \qquad (2)$$

The constants f^* and b^* now involve the dielectric constant ϵ of the dielectric, and χ^* is the work function for the cathode-dielectric system, i.e. the difference between the Fermi level of electrons in the cathode and the electrostatic potential of an electron removed to infinity in the dielectric. It can be shown that $\chi^* < \chi/\epsilon$, but, beyond this, χ^* can be specified only by measurement.

In actual practice, the equation just given probably does not apply at all. If the dielectric is crystalline so that its electron states are distributed in bands, then a different kind of barrier to emission arises, whose shape depends on the concentration and nature of impurities in the crystal.(5) Something similar may occur in amorphous solids and liquids; furthermore, the mean free path may be so short in these substances that the whole basis for the derivation of the electron emission laws is invalidated.

Nevertheless, the field-emission current should depend on the field in an exponential way, and the equation

$$j = a \exp(-b/E),$$

with empirical constants, should be satisfactory.

B. Ion Emission

Experimental evidence to be described in this paper indicates that, under proper conditions, an emission current of ions may be obtained. The experiments involve the use of aqueous electrolyte solutions as cathodes in the study of the breakdown of liquids immiscible with water. We wish to discuss here the nature of the emission, dealing mainly with a simple picture of the process which has to be modified to agree with experiment, but which must be understood in order to interpret the actual results.

In Fig. 2, we have sketched the "motive" (electrostatic potential plus an effective potential due to image forces) of a negative charge in a system consisting of aqueous electrolyte cathode, a dielectric liquid, and a metal anode, in the presence of an electric field. The slight decrease in the motive just to the left of the electrolyte-dielectric interface is due to the distortion of the ionic distribution by the electric field; in contrast to what occurs in metallic conductors, the field must extend an appreciable distance into the cathode. The rise to the right of the interface is due to an assumed increase in energy of the ions as they move from the water layer to the dielectric layer, and the shape of the curve in this region is prescribed by the image force between the ion and the electrolyte.

Calculation shows that for as low a concentration of ions as 10^{-4}N, the drop in potential in the electrolyte is less than 0.25 volt out of 10 kilovolts impressed across 0.01 cm of dielectric. This drop will be ignored henceforth.

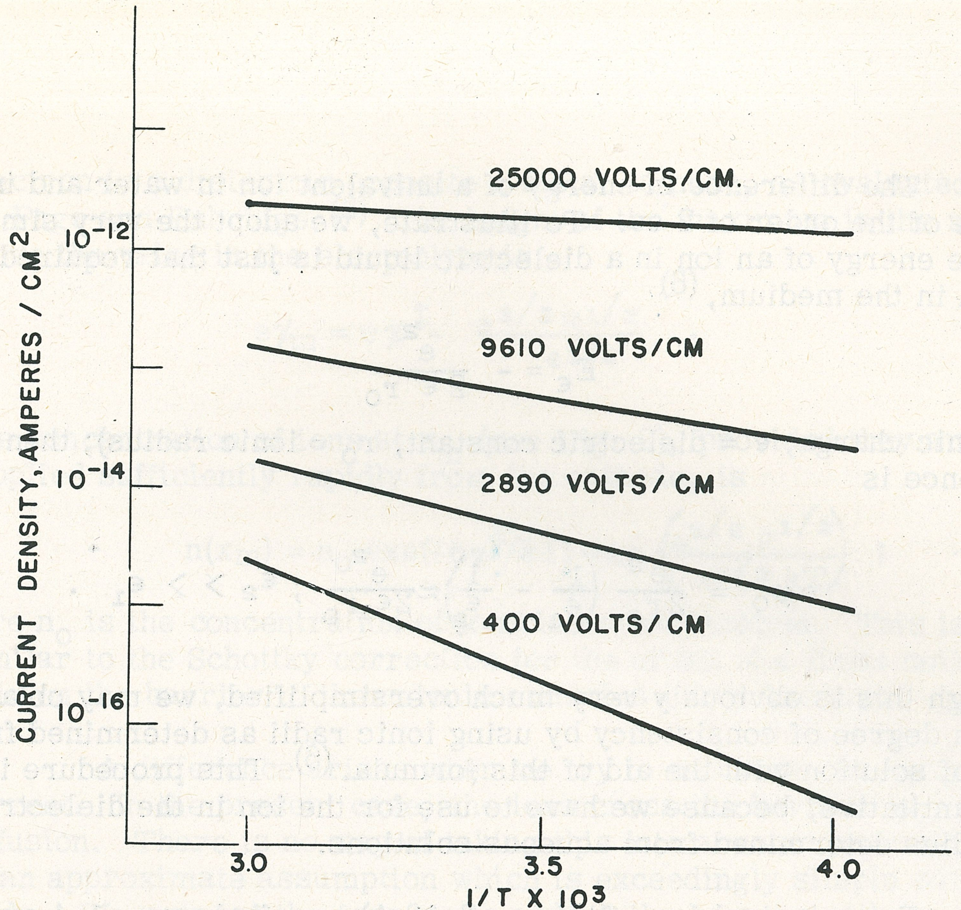

Fig. 1 Currents in toluene at various field strengths as a function of temperature (after Le Page and Dubridge).

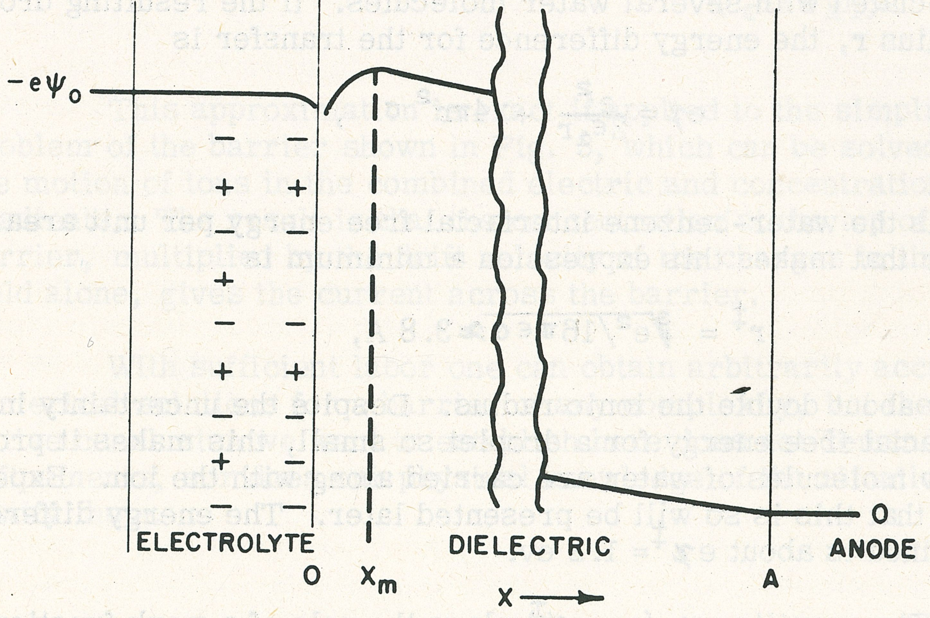

Fig. 2 Motive of negative charge in electrolyte dielectric system.

The difference in energy of a univalent ion in water and in benzene may be of the order of 2 ev. To illustrate, we adopt the very simple view that the energy of an ion in a dielectric liquid is just that required to charge the ion in the medium, (6)

$$E_\epsilon = -\frac{e^2}{2\epsilon r_o} \qquad (3)$$

(e = ionic charge, ϵ = dielectric constant, r_o = ionic radius); then the energy difference is

$$e\chi_o = \frac{e^2}{2r_o}\left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2}\right) \approx \frac{e^2}{2\epsilon_1 r_o}\,;\ \epsilon_2 >> \epsilon_1\,. \qquad (4)$$

Although this is obviously very much oversimplified, we may obtain a certain degree of consistency by using ionic radii as determined from heats of solution with the aid of this formula. (6) This procedure is still not quantitative, because we have to use for the ion in the dielectric, the radius determined from aqueous solutions.

For a typical ion, Cl^- (r_o = 2.13 A), we find $e\chi_o$ = 1.4 ev for the water-benzene transfer.

There is the possibility that the ion may enter the dielectric still associated with several water molecules. If the resulting droplet has a radius r, the energy difference for the transfer is

$$e\chi = \frac{e^2}{2\epsilon_1 r} + 4\pi r^2\sigma\,, \qquad (5)$$

where σ is the water-benzene interfacial free energy per unit area. The value of r that makes this expression a minimum is

$$r^\ddagger = \sqrt[3]{e^2/16\pi\epsilon\sigma} \approx 3.8\ \text{A},$$

a number about double the ionic radius. Despite the uncertainty in using an interfacial free energy for a droplet so small, this makes it probable that a few molecules of water are carried along with the ion. Experimental evidence that this is so will be presented later. The energy difference thus obtained is about $e\chi^\ddagger$ = 1.2 ev.

The quantity $e\chi_o$ (or $e\chi^\ddagger$) plays the role of a work function for the ion. The motive for the ion is of the same form as that for an electron in a dielectric opposite a metal cathode, as evaluated by Le Page and Dubridge. (3) The height of the maximum in the motive above the value in the electrolyte is

$$e\chi_m = e\chi^\ddagger - \frac{e^{3/2}E^{1/2}}{\epsilon^{1/2}}\,. \qquad (6)$$

The concentration of ions at x_m (see Fig. 2), provided they are supplied sufficiently rapidly from the cathode, is

$$n(x_m) = n_o \exp(-e\chi^\ddagger/kT)\exp\left(\frac{e^{3/2}E^{1/2}}{\epsilon^{1/2}kT}\right)\,; \qquad (7)$$

here n_o is the concentration of ions in the electrolyte. This is similar to the Schottky correction for the effect of a finite collecting field on the barrier to thermionic emission into a vacuum.

A difference arises when we try to calculate the emission current. In the present case, the ions cross the barrier by diffusion. There is no way of taking this into account precisely, so an approximate assumption which is exceedingly simple will be made. We suppose the ions move across the barrier with the drift velocity μE they would have in the presence of the field E alone. Then we have for the current density

$$j = -\mu e E n_o \exp(e\chi^\ddagger/kT)\exp\left(\frac{e^{3/2}E^{1/2}}{\epsilon^{1/2}kT}\right)\,. \qquad (8)$$

This approximation is exact if applied to the simplified problem of the barrier shown in Fig. 3, which can be solved for the motion of ions in the combined electric and concentration gradients. The result is that the concentration at the top of the barrier, multiplied by the drift velocity of the charges in the electric field alone, gives the current across the barrier.

With sufficient labor one can obtain arbitrarily accurate numerical solutions for a barrier of any complexity, but the qualitative conclusion we want to establish here does not demand such refinements, nor does our physical knowledge of the situation justify them.

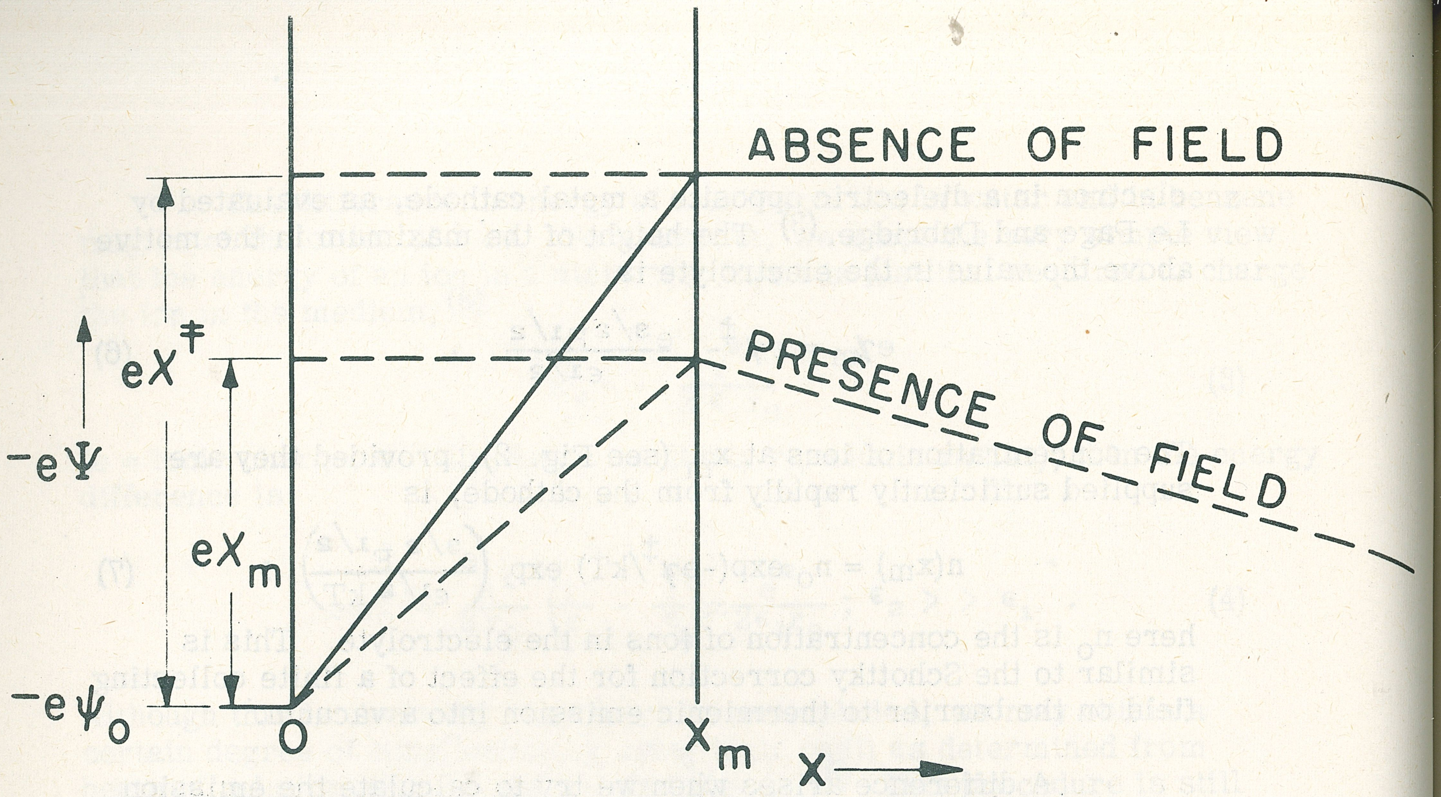

Fig. 3 Potential Barrier for Simplified Emission Problem.

Equation (8) predicts a negligible emission current at any reasonable field strength. The reason is that the Schottky correction

$$\frac{e^{3/2}E^{1/2}}{\epsilon^{1/2}kT}$$

lowers the barrier by only 0.25 volt for a field of 10^6 volts/cm. This implies that the barrier layer is about 25 A thick; a barrier layer of 100 A, on the other hand, gives a correction to $e\chi^{\mp}$ of 1 volt, and an emission current of the order of 0.5 ampere.

We have obtained evidence of emission currents of almost this order of magnitude, but only after one or more preparatory electric pulses. Apparently, the function of the preparatory pulses is to blur the Schottky layer, thus providing enhanced emission. We will simply make the obvious assumption that such an emission current depends exponentially on the electric field.

III. SPACE-CHARGE EQUATIONS

A. Simple Space-Charge Equations

The charge and field distributions in the gap (assumed to consist of two infinite plane conductors separated by a distance of a centimeters)

are governed by the following relationships:

$$\epsilon(d^2\phi/dx^2) = -4\pi\rho ;$$
$$j = -\rho\mu(d\phi/dx), \quad 0 \leq x \leq a . \qquad (9)$$

In these equations, ϵ is the dielectric constant, ϕ the electrostatic potential, μ the charge mobility, j the current density, ρ the charge density, and x the coordinate (which varies from 0 to a across the gap). We consider only negative charge, so that μ and ρ are negative. For the moment, we assume that the mobility is independent of the electric field. The consequences of any failure of this assumption will be assessed shortly.

The problem is made definite by the statement of certain boundary conditions:

$$\phi = 0 \text{ at } x = 0,$$
$$\phi = \phi_o \text{ at } x = a,$$
$$-(d\phi/dx) = E_c \text{ at } x = 0. \qquad (10)$$

The first two conditions always obtain. The simplest assumption about the third is that $E_c = 0$, and the solutions corresponding to this boundary condition are the following:(7)

$$\phi = \phi_o x^{3/2}/a^{3/2},$$
$$\rho = (3/32\pi)\ (\epsilon\phi_o/a^{3/2}\ x^{1/2}),$$
$$j = (9\epsilon\mu\phi_o^2/32\pi a^3). \qquad (11)$$

These are analogues of the Langmuir-Childs equations, valid, however, for liquids, solids, and high-pressure gaseous dielectrics. A consequence of the first of these is that the electric field at the anode, E_a, is the average field $E_o = \phi_o/a$ increased by a factor 3/2.

B. The Self-Consistent Solution

One of the results of the simple model is that a finite current flows through the gap. The solution is thus obviously not self-consistent, since the assumption $E_c = 0$ implies that the field-induced emission current is zero. The boundary condition must be so adjusted that the current flowing in the gap, as derived from the space-charge equations, is equal to the emission current of the cathode given by its field-emission law.

We must therefore solve Eqs. (9) under the general boundary condition $-(d\phi/dx)_{x=0} = E_c$. We will then regard E_c as a function of j in the solutions. The integrations, together with appropriate determination of the constants arising, give now

$$\phi = \frac{2}{3}\frac{\epsilon\mu}{8\pi j}\left[\left(\frac{8\pi j}{\epsilon\mu}x + E_c{}^2\right)^{3/2} - E_c{}^3\right]. \tag{12}$$

This and succeeding results reduce to the simple space-charge equations if we set $E_c = 0$.

The current is derived by putting ϕ equal to ϕ_o when x equals a. The implicit equation for j is then

$$\phi_o = \frac{2}{3}\frac{\epsilon\mu}{8\pi j}\left[\left(\frac{8\pi aj}{\epsilon\mu} + E_c{}^2\right)^{3/2} - E_c{}^3\right]. \tag{13}$$

In terms of convenient dimensionless quantities, $\gamma_c = E_c/E_o$ and $\eta = \frac{8\pi aj}{\epsilon\mu E_o{}^2}$, this equation becomes

$$\eta = \frac{2}{3}\left[(\eta + \gamma_c{}^2)^{3/2} - \gamma_c{}^3\right]. \tag{14}$$

Table I gives solutions of this cubic equation for η, for various values of γ_c.

TABLE I

γ_c	0	0.20	0.40	0.60	0.80	1.00
η	2.25	2.14	1.84	1.35	0.70	0.00
γ_a	1.50	1.48	1.41	1.31	1.16	1.00

In addition to the reduced current η, the table lists values of the reduced anode field $\gamma_a = E_a/E_o$ obtained by differentiating Eq. (12) with respect to x and then setting x equal to a. As previously, if the cathode field is made to be zero, the anode field is three-halves of the average field. On the other hand, if γ_c is 1.0, then γ_a is 1.0 also.

Equation (14) gives a relation between the reduced current and the reduced cathode field which arises from consideration of the transport of charge through the dielectric. There is another equation connecting them: namely, the cathode emission law

$$\eta = \eta(\gamma_c, E_o). \tag{15}$$

For a given average field E_o, Eqs. (14) and (15) can be solved simultaneously to give numerical values of the reduced current and cathode field, and hence the reduced anode field.

In Fig. 4, we have drawn a typical cathode emission characteristic and the space-charge-limited current as a function of field strength, to illustrate the meaning of these results. The assumed cathode characteristic has the form given by Eq. 15 and is plotted against E_o. In the region $E_o < E_1$, emission is so feeble that γ_c 1, and the field is essentially undistorted. Note that our self-consistent solution follows the cathode characteristic in this region. At some field E_1, the reduced emission current has grown to, say, 0.2, and Table I shows that appreciable deviations of γ_a and γ_c occur. As E_o is further increased, the strong tendency of the emission current to increase rapidly forces the system over into space-charge-limited conditions under which the reduced current in the gap is independent of the field (the actual current varies as the square of E_o).

Comparison of these results with those of the preceding section shows that the simple treatment of the problem gives values of the anode field which are asymptotically correct at low and high fields. Consequently, the discussion of the breakdown process to be given later will be developed on the basis of the simple space-charge laws.

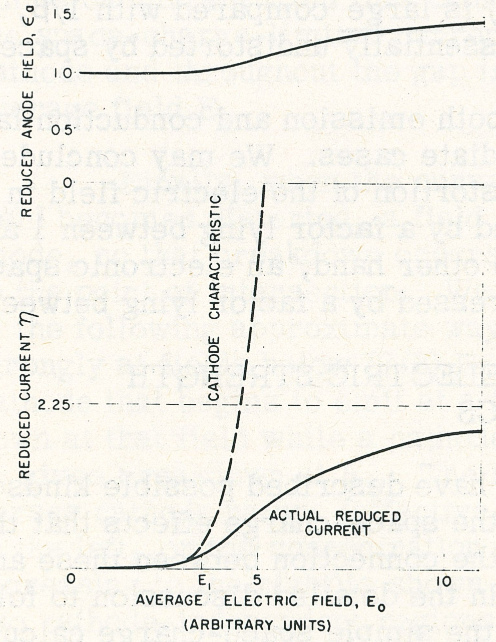

Fig. 4

C. Dependence of the Mobility on the Electric Field

In the discussion just given we have assumed that the mobility of the negative charges is independent of the electric field. This assumption is undoubtedly defective in the field-strength region treated here. Nevertheless, there is no information about the field dependence of electron drift velocities in liquids under high fields. Shockley(8) has used the work of Seitz(9) on the mobility of electrons in crystalline, nonpolar insulators to show that in this case the mobility ought to decrease with electric field at high fields, eventually varying as $E^{-1/2}$. On the other hand, it is possible that an electron in a nonpolar liquid may become trapped or "solvated," and thus behave like a molecular ion, in which case the mobility would be expected to increase with field at high fields (see below). It can be proved that if the mobility varies as $E^{-1/2}$, the anode field under space-charge-limited conditions is 5/3 times the average field.

For ionic charge carriers, the matter is somewhat clearer. It is certain that the drift velocity of such charges will increase strongly with field in the high-field region. Not so certain is the functional form, but a crude approximation to the current, often used, is

$$j = a \sinh (\beta d\Phi/dx);\ a, \beta > 0. \qquad (16)$$

This current deviates from an ohmic law if $\beta\ (d\Phi/dx)$ is not small compared with unity. If Φ_0/a (the average field) is large compared with $1/\beta$, it can be shown that the field in the gap is essentially undistorted by space charge.

Because of uncertainties in both emission and conduction laws, it is not worth while to develop intermediate cases. We may conclude, however, that in practice the extent of distortion of the electric field in the gap due to ionic space charge is expressed by a factor lying between 1 and 1.5, multiplying the average field. On the other hand, an electronic space charge may produce a distortion of field expressed by a factor lying between 1 and 2.

IV. DEPENDENCE OF MEASURED ELECTRIC STRENGTH ON CATHODE CHARACTERISTICS

In the previous sections, we have described possible kinds of field-dependent charge emission and the space-charge effects that they may produce. We have still to show the connection between these and measurements of electric strength. In the detailed discussion to follow, we will use principally the results of the simple space-charge calculation. The modification that may be made by a more refined treatment will be indicated afterward.

In Fig. 5, we have plotted some current densities versus electric field strength. The solid lines represent the emission characteristics of a hypothetical series of cathodes as a function of the field strength at the cathode surfaces; the emission described by these curves is supposed to increase exponentially with electric field. The dotted curve is the space-charge-limited current plotted against the average field in the gap.

Consider first the cathode curve marked I. If such a cathode is used, an increase in the applied electric field will bring about an increase in the emission current, following along the solid curve until it intersects the dotted one. Beyond this point, the potential emission current of the cathode is larger than can be collected. The actual current therefore follows the dotted line thenceforth; the emission is "space-charge-limited," and the field in the gap is no longer uniform. The simple space-charge law states that, in this situation, the maximum field in the gap (that at the anode) is three-halves the average field. Thus, when we have progressed to the right in Fig. 5 until the average field is two-thirds the intrinsic strength, breakdown will occur. This is true of any cathode whose characteristic intersects the dotted curve at a field less than (2/3) E_i, where E_i is the intrinsic strength of the dielectric.

Next, we consider the cathode curve marked III. The emission current from this cathode at the field E_i is still below the space-charge-limited current. Consequently, the field on the cathode and throughout the gap is E_i, and breakdown occurs at the average field E_i.

Finally, when the curve II intersects the dotted line and the field becomes distorted, a field greater than E_i is produced at the anode, so that breakdown occurs when the average field corresponds to the point of intersection. We can describe the entire situation in the following approximate way: any cathode that begins to emit strongly at fields below (2/3) E_i gives breakdown at (2/3) E_i. A cathode that begins to emit at a field between (2/3) E_i and E_i gives breakdown at that field while a cathode whose emission is negligible below E_i gives breakdown at E_i. The resulting plot of breakdown strength versus cathode nature (effective work function of a metal increasing to the left, or the concentration of an aqueous electrolyte cathode increasing to the right) is shown in Fig. 6, and is characterized by two cathode-independent regions (the upper and lower flat portions) and a transition region.

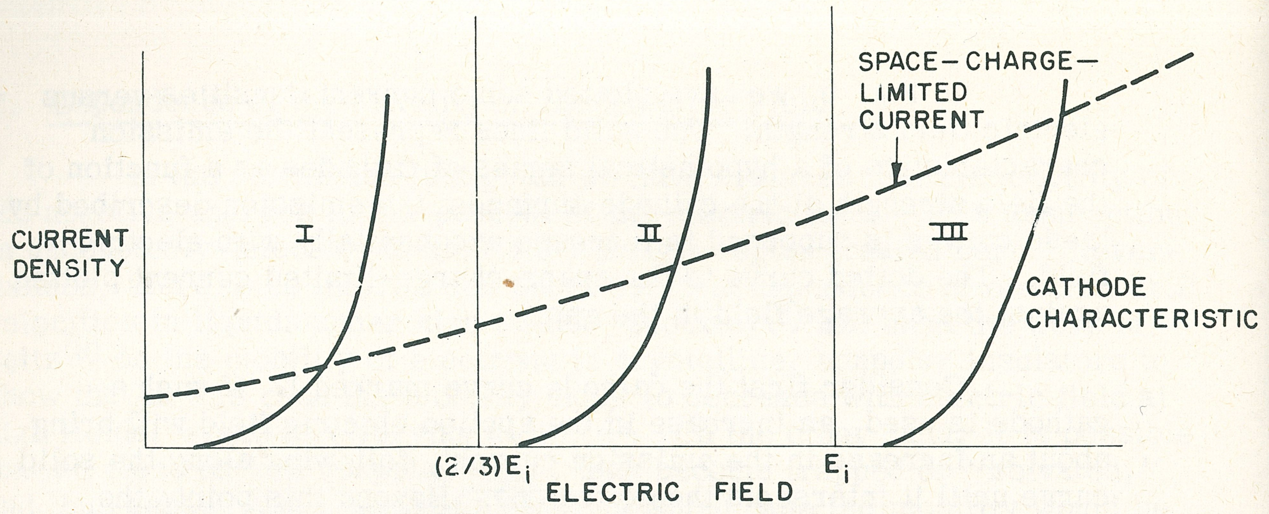

Fig. 5

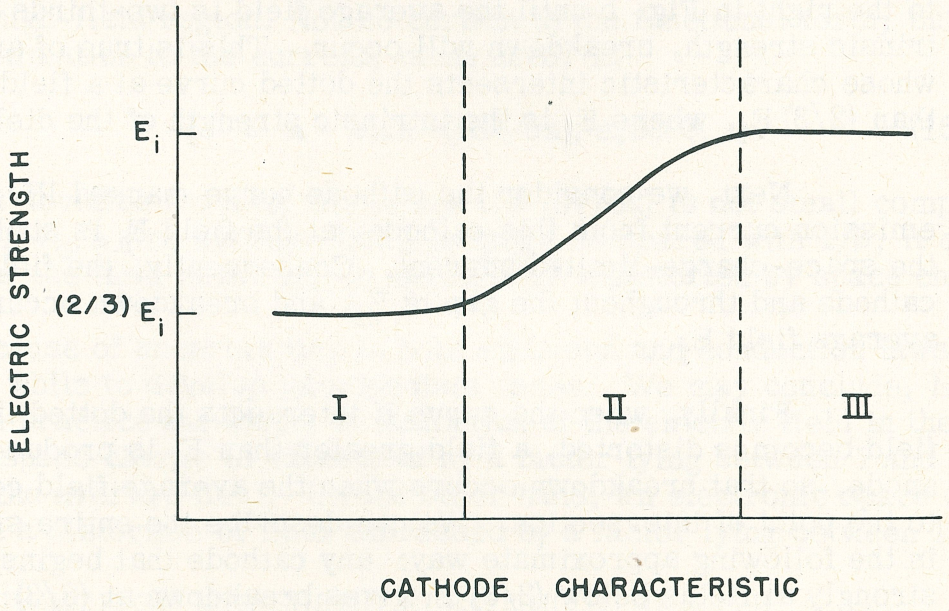

Fig. 6

The equation of the transition curve is obtained by equating emission current and space-charge-limited current; if we treat the latter as constant compared with the rapidly changing emission current, we obtain, in the case of ion emission,

$$n_o \exp(aE^{\theta}) = \text{constant},$$

or

$$E^{\theta} = \frac{1}{a}(\text{constant} - \log n_o). \qquad (17)$$

Here θ is a constant near unity (if the emission were of the Schottky type, it would be one-half). Thus, the breakdown field should vary approximately linearly with the logarithm of the concentration in the intermediate portion of the graph of Fig. 6.

One modification of the results of this section, introduced by more detailed space-charge considerations, should be mentioned. The relation which the upper and lower flat portions of the curve of Fig. 6 bear to each other depends on the law relating the drift velocity of the charge carrier to the electric field. In Section III, we saw that for electrons this relationship is not understood, so that no predictions can be made about the ratio of the two flat portions if the cathodes used are metals.

On the other hand, if the cathode emits ions, we can say with confidence that the drift velocity varies at least as strongly as the first power of the field. So, according to the results of Section III, the ratio of the fields given by the upper and lower flat portions must lie between one and three-halves.

V. EXPERIMENTAL METHODS

In practice, we are usually concerned with metallic cathodes, but any detailed theory of their effects is difficult to develop and impossible to verify experimentally at present. We have developed a theory for the ion-emitting cathode because it runs parallel to that for an electron-emitter, and at the same time is susceptible to a detailed experimental study. We will now report the results of our experiments with such ion-emitting cathodes.

A. Experimental Techniques

The experiments were carried out with a rectangular pulse generator which delivers single, well-defined, rectangular voltage pulses of variable amplitude and duration. Amplitudes up to fifteen kilovolts may be obtained, with durations ranging from 0.25 to 54 microseconds. The use of such pulses should essentially eliminate erroneous results due to local, prebreakdown heating of the spark gap. This effect, giving rise to what is know as "thermal breakdown," has often been observed in systems to which d-c and a-c voltages were applied. This is obviously undesirable if one is attempting to study the fundamental mechanism of breakdown.

The construction details of the breakdown cell are shown in Fig. 7. The general design is similar to that used by Bahre,(10) except that one electrode is made movable through the use of a bellows and micrometer drive arrangement. The cell is equipped with optical windows to make it possible to monitor the breakdown during an experiment and to adjust the gap spacing by optical means. The ball and socket arrangement for the upper electrode is provided in order that a single solid electrode may be used for a number of experiments, a fresh part of its surface being used for each one. For the present series of experiments, the cell was used in the vertical position, and a glass cup filled with aqueous electrolyte substituted for the lower electrode.

Benzene was chosen as the dielectric for the measurements because of its ready availability in a relatively pure condition, and because of its immiscibility with water. The material used was Baker and Adamson (c.p.) thiophene-free benzene; no attempt was made to purify it further. The benzene was filtered through an ultrafine (0.9 to 1.4 μ pore size) fritted glass filter to remove solid particles.

After assembly of the dielectric-electrode system, the traveling microscope (32 X) was focused on the gap through the optical windows of the cell (Fig. 8). The gap was illuminated with the microscope illuminator. The electrode spacing of 0.0084 ± 0.0001 cm was set using the interference colors that appeared when the electrode separation was very small; we used a particular red color that corresponded to a separation of 0.0008± 0.0001 cm. From this point, the spacing was increased by 0.0076 cm, as read from the micrometer, to its final value of 0.0084 cm.

Two techniques were used for making the electric strength measurements. The first, hereafter referred to as the "many-pulse" technique, consisted of the application of single, constant-length, rectangular pulses of gradually increasing amplitude, until disruption of the dielectric occurred. In the second method, only one pulse, near breakdown, was applied to the cathode-dielectric-anode system. If breakdown did not occur, a pulse of slightly higher voltage was applied to the next, completely new system.

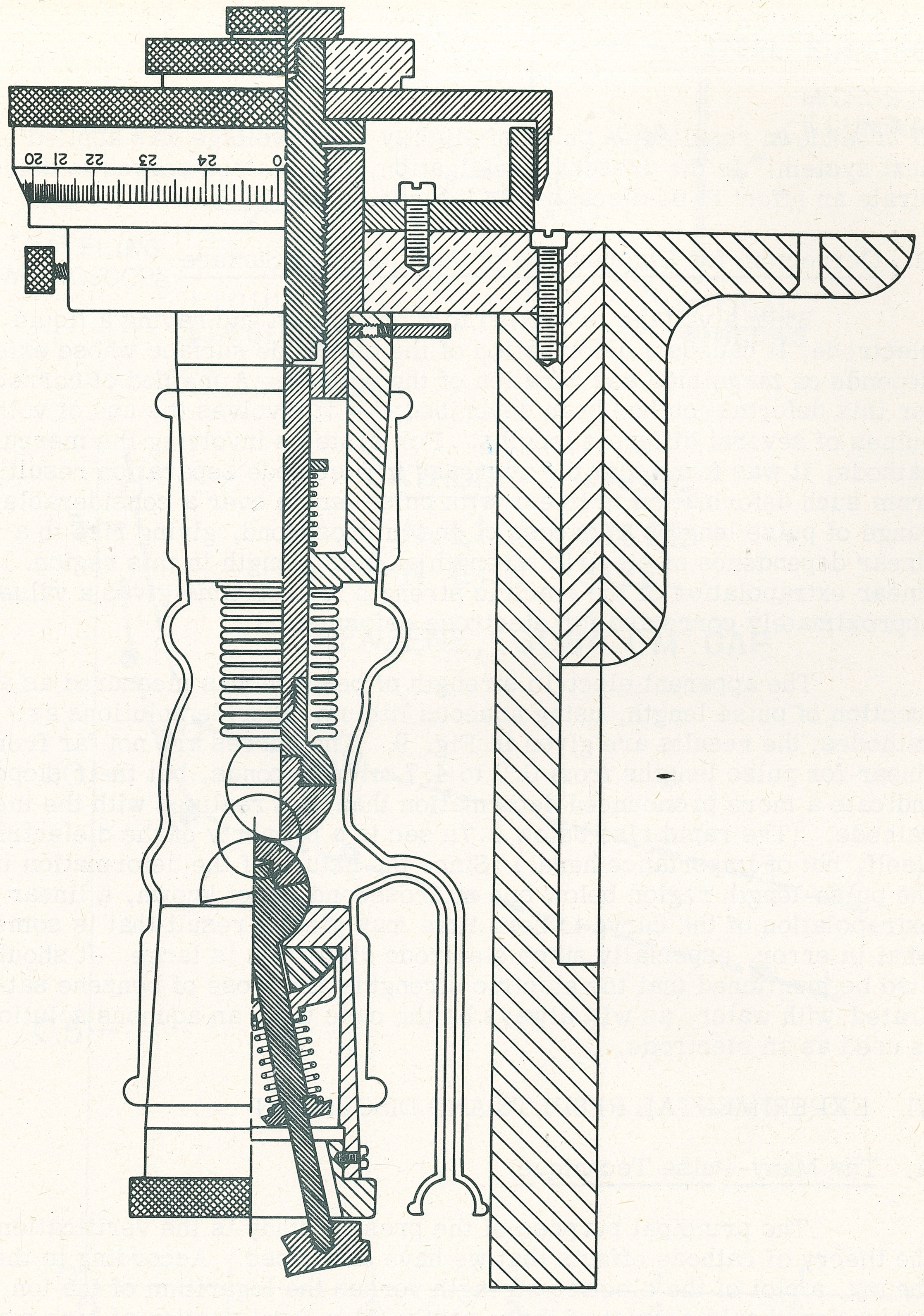

Fig. 7 Assembly of breakdown cell.

If breakdown resulted, a pulse of slightly lower voltage was applied to the next system. In the present investigation, this method served to demonstrate an effect to be discussed in later sections.

B. Correction for Deformation of the Electrode Surface

When a voltage is applied to a breakdown gap having a liquid electrode, it causes a deformation of the electrode surface whose extent depends on magnitude and duration of the voltage. A method of correction for this deformation has been described;(11) it involves the use of voltage pulses of several different lengths. For systems involving the mercury cathode, it was found that the decrease in electrode separation resulting from such deformation is linear with pulse length over a considerable range of pulse lengths in excess of one microsecond, giving rise to a linear dependence of electric strength on pulse length in this region. A linear extrapolation of the electric strength to zero time gives a value approximately corrected for electrode deformation.

The apparent electric strength of benzene was measured as a function of pulse length, using aqueous lithium chloride solutions as cathodes; the results are given in Fig. 9. The curves are not far from linear for pulse lengths from 0.7 to 4.7 microseconds, but their slopes indicate a more pronounced deformation than was realized with the mercury cathode. (The rapid rise below 0.7µ sec is a property of the dielectric itself, not of importance here.) Since the nature of the deformation in the pulse-length region below one microsecond is not known, a linear extrapolation of the curve to zero time may yield a result that is somewhat in error, especially since electrode distortion is large. It should also be mentioned that the electric strengths are those of benzene saturated with water, as will always be the case when an aqueous solution is used as an electrode.

VI. EXPERIMENTAL RESULTS AND DISCUSSION

A. The Many-Pulse Technique

The principal purpose of the present study is the verification of the theory of cathode effects that we have described. According to the theory, a plot of the electric strength versus the logarithm of the ion concentration should consist of three parts: (1) a level portion at high concentrations, (2) a linear increase over an intermediate concentration range, and (3) another level portion at low concentrations.

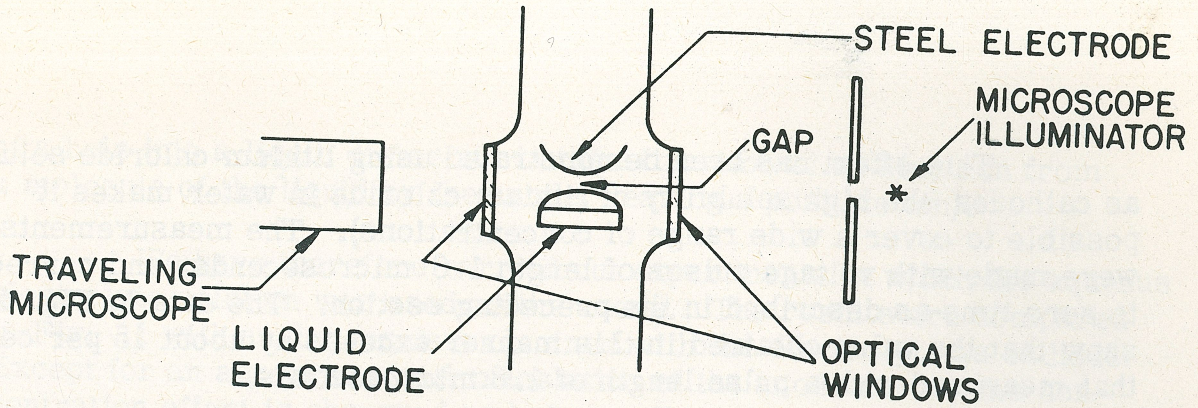

Fig. 8 Assembly for setting gap.

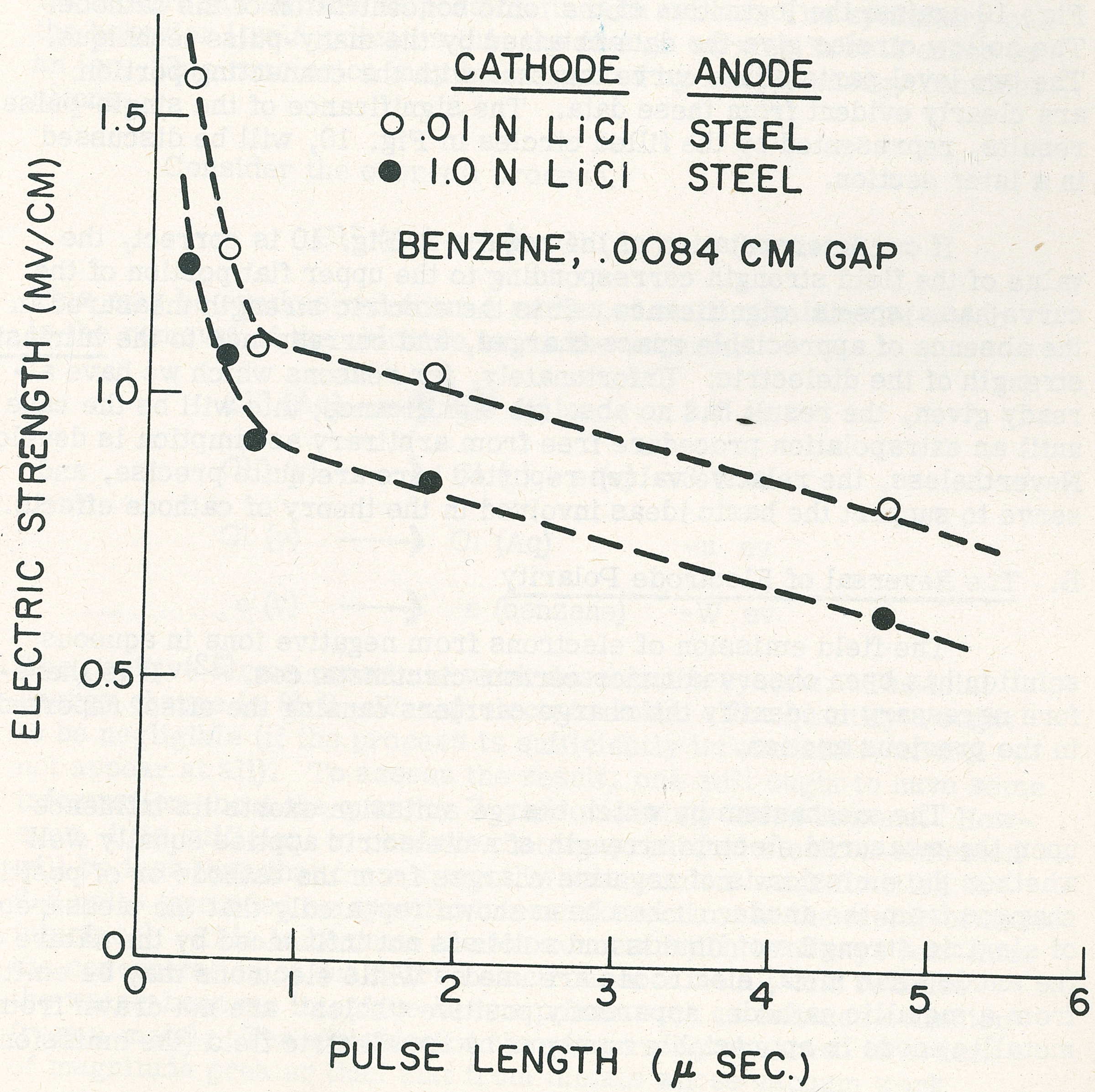

Fig. 9 Dependence of the electric strength of benzene upon pulse length.

This effect has been demonstrated using lithium chloride solutions as cathodes (the high solubility of lithium chloride in water makes it possible to cover a wide range of concentrations). The measurements were made with voltage pulses of length 1.8 microseconds, and corrected to zero time as described in the preceding section. The data in Fig. 9 show that the value obtained in this manner exceeds by about 15 per cent that measured with a pulse length of 1.8 microseconds.

The electric strengths measured in this study are plotted in Fig. 10 against the logarithm of the ionic concentration of the cathode. The hollow circles give the data obtained by the many-pulse technique. The two level parts of the curve together with the connecting portion are clearly evident from these data. The significance of the single-pulse results, represented by the filled circles in Fig. 10, will be discussed in a later section.

If our interpretation of the results in Fig. 10 is correct, the value of the field strength corresponding to the upper flat portion of the curve has a special significance. It is the electric strength measured in the absence of appreciable space charges, and corresponds to the intrinsic strength of the dielectric. Unfortunately, for reasons which we have already given, the result has no absolute significance; this will be the case until an extrapolation procedure free from arbitrary assumption is developed. Nevertheless, the relative values reported here are quite precise, and serve to support the basic ideas involved in the theory of cathode effects.

B. The Reversal of Electrode Polarity

The field emission of electrons from negative ions in aqueous solution has been observed under certain circumstances.(12) It is therefore necessary to identify the charge carriers causing the effect reported in the previous section.

The mechanism by which charge emission exerts its influence upon the measured electric strength of a dielectric applies equally well whether the emission is of negative charges from the cathode or of positive charges from the anode. It has been shown repeatedly that the measurement of electric strengths of liquids and solids is not influenced by the nature of the anode when metal electrodes are used. While electrons may be emitted from a metallic cathode, apparently positive "holes" are not drawn from a metallic anode in appreciable numbers by the electric field (the emission of a hole into a liquid dielectric is the extraction of an electron from a molecule of the liquid by the anode, leaving a positive ion).

We have therefore carried out experiments in which the aqueous electrolyte solution was used as the anode. The results are compared in Fig. 11 with analogous data obtained with the electrolyte as cathode. Except for an apparent small translation of the anode curve, the concentration effect is observed as before. Because of the close correspondence between the two curves, we must assume that emission from the electrolyte surface is possible in both cases. The symmetry of the behavior itself indicates that the charge carrier in both cases is an ion. This conclusion may be supported by simple energy considerations.

Consider the over-all process,

$$\mathrm{Cl^-\ (Aq)} \longrightarrow \mathrm{Cl\ (Aq') + e\ (benzene)}.$$

This may be synthesized from a series of steps, the first of which is the removal of the chloride ion to the vacuum:

$$\begin{array}{lcll}
\mathrm{Cl^-\ (Aq)} & \longrightarrow & \mathrm{Cl^-\ (v)} & 3.0\ \mathrm{ev} \\
\mathrm{Cl^-\ (v)} & \longrightarrow & \mathrm{Cl\ (v) + e\ (v)} & 3.8\ \mathrm{ev} \\
\mathrm{Cl\ (v)} & \longrightarrow & \mathrm{Cl\ (Aq)} & -u\ \mathrm{ev} \\
\mathrm{e\ (v)} & \longrightarrow & \mathrm{e\ (benzene)} & -W\ \mathrm{ev}
\end{array}$$

The positive terms constitute work done on the system. The total energy change is (6.8 - W - u) electron volts. The quantity u ought to be negligible (if the process is sufficiently irreversible, it will not appear at all). To assess the result, one still ought to have some information about the quantity W ; unfortunately there is none. However, it is sufficient to observe that the predicted electron emission will be less than that from a metal whose vacuum work function is 6.8 volts (provided no specific interaction occurs at the metal-benzene interface). This is because the ion concentration is always less than the concentration of quasi-free electrons in a metal, and because the water-benzene interface has no points such as enhance emission from a metal. The emission of charge actually observed is orders of magnitude greater than that from metals whose vacuum work functions range from 4 to 5 electron volts.

C. The Nature of the Ion

In a separate series of experiments we have investigated the behavior of cathodes containing various negative ions. These experiments were performed with the 0.25-microsecond pulse, using the many-pulse technique, and the results (not corrected for deformation) are reported in Fig. 12. It is clear that the nature of the negative ion has little or no influence on the effect studied here.

There are two conclusions that may be drawn from this result. As an observation supplementary to the discussion of the preceding section, we may say that, if electron emission were to occur, the effect of the widely different electron ionization energies of the hydroxyl ion and chloride ion should have been observed (this difference is about 2 electron volts for the gaseous ions). Secondly, as we have had occasion to comment, it is likely that several water molecules accompany the ion in its transfer to the benzene. This will have the result that the effective ion sizes are about the same, a conclusion in harmony with the experimental results.

D. The Single-Pulse Technique

When aqueous electrolyte cathodes of concentration lower than 10^{-2} N were used in the breakdown studies of benzene, the application of pulses near breakdown invariably resulted in the appearance of a cloud of small particles (1 to 5 microns in diameter) in the gap. Since these particles could not easily be removed between pulses, erroneous breakdown values often resulted. It was therefore necessary to use the single-pulse technique with systems involving these low cathode concentrations.

An extension of this technique to systems in which cathodes of higher concentration were used has demonstrated another interesting effect. The results, plotted in Fig. 10, show that the dependence of the electric strength on concentration has disappeared. The single-pulse strength obtained with any cathode whose concentration is greater than 10^{-3} normal is equal to the value obtained from the upper flat portion of the many-pulse curve. Evidently, a single pulse is incapable of inducing ion emission. The function of the pulses preceding breakdown, when the many-pulse technique is used, is then to "blur" the Schottky barrier, which is initially too narrow to allow appreciable emission. Although it is impossible to say exactly what the prebreakdown pulses do, it is probable that they create something like an emulsified layer about 100 A thick at the interface. In the presence of the electric field, the barrier presented by this layer may be lowered as much as one volt, making intense emission

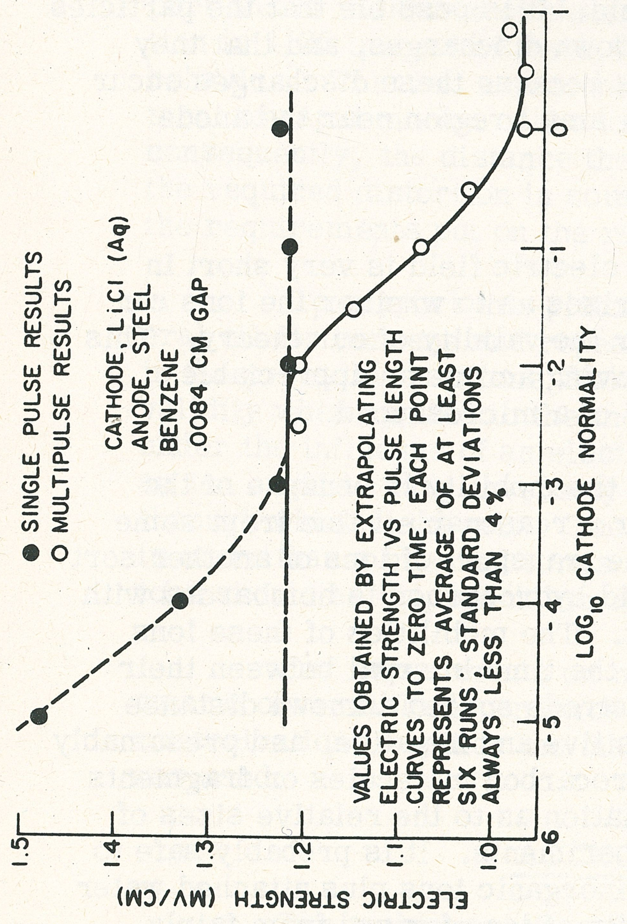

Fig. 10 Dependence of the corrected electric strength of benzene upon cathode normality.

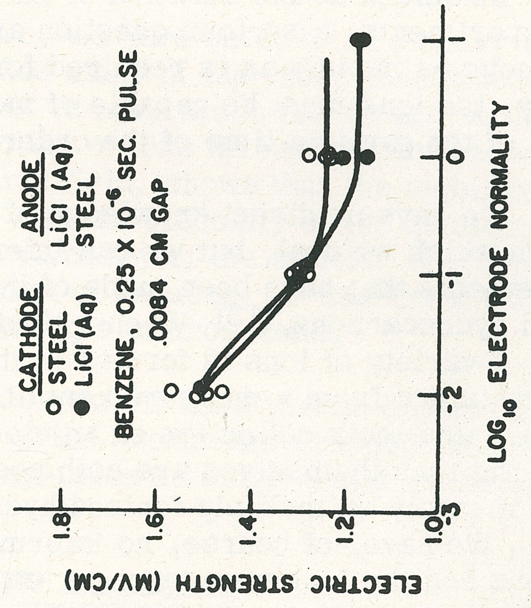

Fig. 11 The effect of reversal of electrode polarity upon the electric strength of benzene.

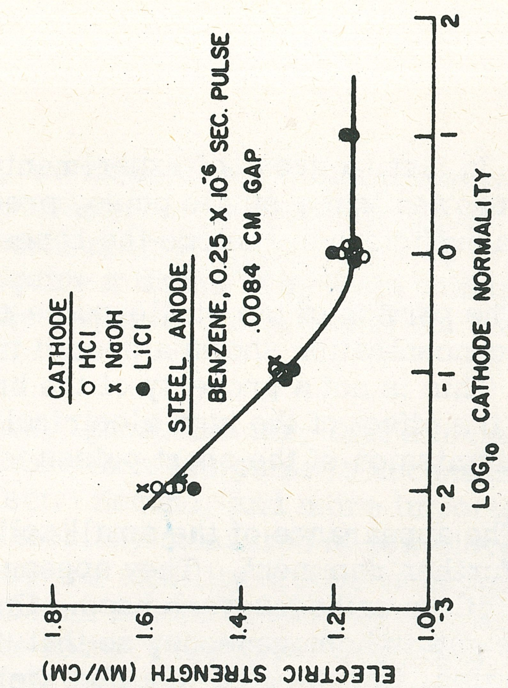

Fig. 12 The effect of the nature of the ion upon the electric strength of benzene.

possible. In fact, a group of experiments involving a "double-pulse" technique showed that a single pulse, preceding the breakdown pulse itself, was sufficient to restore the concentration effect almost completely.

The portion of the single-pulse curve in Fig. 10 that lies below 10^{-3} N in concentration shows a second increase in apparent electric strength. This is not a property of the breakdown system at all, but is caused by the effect of the high electrical resistance of these solutions on the transmission of the short pulses to the breakdown gap.

The appearance of the small solid particles mentioned earlier deserves further comment. They appeared during pulses near breakdown when very dilute cathodes were used. Under such conditions, the electric field in the gap is homogeneous, so that the entire dielectric, rather than a small region, is subjected to a high field. It is possible that the particles are bits of carbon produced by prebreakdown discharges, and that they show up under the present circumstances because these discharges occur throughout the dielectric rather than in a small region near the anode.

E. The Motion of the Ions

Inasmuch as the duration of the electric field is very short in these experiments, a serious question arises as to whether the ions can really move as rapidly as is required for the validity of our theory. This is to say, the ions must be capable of moving across an appreciable fraction of the gap in a time of the order of a microsecond.

We have no direct knowledge of the mobility in benzene of the ions with which we deal, but we can infer a reasonable value from some measurements that have been made of the transport of ions of another sort in liquid hydrocarbons.(13) When a liquid hydrocarbon is bombarded with X-rays, a variety of ions is formed in it. The mobilities of these ions may be obtained from a measurement of the time interval between their production and their collection on an electrode spaced a known distance away. The ions themselves are both positive and negative, and presumably consist of singly or multiply ionized hydrocarbon molecules or fragments thereof. We have, of course, no information as to the relative sizes of these ions and the ions we use in our experiments. It is probably safe to infer that the mobility in benzene of the inorganic ions plus attached water molecules is comparable with the mobility of ions formed from fairly large hydrocarbon molecules, e.g. n-hexane. In this case, the mobilities of the several kinds of carriers were grouped about a value of 5×10^{-4} cm^2/volt second.(12)

Using this mobility, we find that an ion may travel 5×10^{-4} centimeters in a microsecond when the electric field is 10^6 volts/cm. This distance is about 6 per cent of the gap spacing used in our experiments, whereas we require a travel of at least one-third of the gap in order to provide the required distortion of the electric field.

There are two factors, ignored so far, that alleviate this situation. The first is that more than one pulse is necessary to provide the concentration effect. Second, and more important, in this estimate we have used a mobility measured at low electric fields. As pointed out earlier, the mobility of ions is expected to increase with electric field at high fields. Evidence that this is so is provided by the fact that the ratio of the upper and lower flat portions of the curve of electric strength versus cathode concentration is 1.25 instead of the 1.5 ratio that would result from ohmic behavior. This has a secondary effect that also lessens the requirement of rapid motion of the ions. There is less field distortion; consequently, the distance the ions must travel in order to produce the required distortion is somewhat less. Altogether, it seems that the requirements put on the rapidity of ion motion are not excessive.

To support this picture, we have substituted a heavy mineral oil for benzene and repeated many of the experiments described in the preceding sections. Stokes's law, which has an approximate validity when applied to the motion of ions through a viscous medium under the influence of an electric field, shows that the mobility of an ion ought to vary inversely with the viscosity of the medium through which it travels. The viscosity of the mineral oil in question is more than a hundred times that of benzene, so that the motion of ions should be inappreciable during a microsecond.

Our experiments on mineral oil show this to be so. There was no observable dependence of the breakdown strength upon cathode concentration, whether the many-pulse or single-pulse technique was used.

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REFERENCES

(1) A. von Hippel and R. S. Alger, Phys. Rev., 76, 127 (1949).

(2) B. Salvage, Proc. I.E.E., 98, 227 (1951).

(3) W. R. Le Page and L. A. Dubridge, Phys Rev., 58, 61 (1940).

(4) R. H. Fowler and L. Nordheim, Proc. Roy. Soc. (London), A119, 173 (1928).

(5) See, for example, H. C. Torrey and C. A. Whitmer, Crystal Rectifiers, Massachusetts Institute of Technology, Radiation Laboratory Series, McGraw-Hill (1948).

(6) M. Born, Z. Physik, I, 45 (1920).

(7) See, for example, J. D. Cobine, Gaseous Conductors, McGraw-Hill (1941), p. 128.

(8) W. Shockley, Phys. Rev., 82, 330A (1951).

(9) F. Seitz, Phys. Rev., 76, 1376 (1949).

(10) W. Bahre, Archiv. Elektrotechnik, 31, 141 (1937).

(11) A. H. Sharbaugh, R. W. Crowe, and J. K. Bragg, J. Applied Phys., 24, 814 (1953).

(12) A. Guntherschulze and H. Betz, Elektrolyt-kondensatoren, M. Krayn, Berlin (1937).

(13) I. Adamczewski, Ann. Phys., 8, 309 (1937).

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